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NOVEL FIBER PREFORMS: RARE EARTH DOPING(U) BROWN UNIV
PROVIDENCE RI DIV OF ENGINEERING T F MORSE 31 MAR 87
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<p>Optical fibers doped with rare earth elements have potential application as passive fiber devices through their ability to rotate the plane of polarization in the presence of a magnetic field. Such devices have use not only as sensors of electric and magnetic fields but also as fiber lasers for a host of application. The Laboratory for Lightwave Technology, in conjunction with the Dept. of Chemistry, has engaged in a program of the study of rare earth elements in fibers, and in bulk glasses as well. Some of the first rare earth glasses made with the sol-gel technique come from this research.</p>			
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DIVISION OF ENGINEERING

AFOSR-TR-87-0556

March 31, 1987

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Dr. H. Schlossberg
Department of the Air Force
Air Force Office of Scientific Research (AFSC)
Bolling Air Force Base
Washington, DC 20332-6448

Dear Dr. Schlossberg:

Enclosed is the scientific report on grant AFOSR-85-0304.

Sincerely yours,

T. F. Morse
T. F. Morse
Professor of Engineering

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Final Report: Grant AFOSR-85-0304

Novel Fiber Preforms: Rare Earth Doping

August 31, 1985-October 31, 1986

T.F. Morse, Professor of Engineering, Brown University

Division of Engineering, Providence, R.I. 02912

Within the Division of Engineering at Brown University there has been established a Laboratory for Lightwave Technology that involves a multidisciplinary research in a variety of topics. (See Appendix). Equipment grants from the National Science Foundation, from the Department of Defense, and from the Bell Communications Research Laboratory have been responsible for the growth of this facility. Perhaps the key equipment grant was from the Department of Defense that permitted the acquisition of a complete optical fiber draw facility that is just now being set up. The preform deposition facility has been in operation approximately six months, and the experience gained in "debugging" this equipment will prove invaluable in future experiments. With the new draw tower to complement our MCVD vapor deposition capability, we can now design preforms, fabricate them, and pull the final preform into a state-of-the-art optical fiber. We are in contact with several researchers at various Air Force Laboratories (Major J. Rotge, Frank J. Seiler Research Laboratory, USAF Academy, and Dr. A. Yang, Geophysics Laboratory, Hanscomb AFB). In particular, we plan closer collaboration in the future with Major Rotge. One new aspect of research will be to study the recent, as yet unexplained, phenomenon of second harmonic generation in amorphous optical fibers.

The work cited in this report consists of a collaborative effort between Prof. T.F. Morse, Director of the Laboratory for Lightwave Technology, and Prof. W. Risen, of the Brown University Department of Chemistry. Prof. Risen is an expert in glasses, and his

knowledge of the structure of glasses has strengthened our program with regard to work on the rare earth glasses.

In one aspect of the research we have attempted to investigate novel techniques for doping optical fiber preforms with elements that show interesting characteristics for fiber uses as passive or active devices. In particular, we have attempted to examine techniques for the incorporation of rare earth elements into optical fiber preforms. This has been done with the double burner technique proposed by the group at Southampton, and future experiments with axial laser heating of terbium metal are planned. As noted, much of the effort during this initial stage of the research was spent in becoming familiar with the sophisticated equipment now at our disposal.

Although several preforms have been doped with terbium, in our learning to control the doping concentration, we have observed bands of undesired microcrystallinity in some terbium doped preforms. For this reason, these preforms have not been sent off to be drawn and analyzed. The group at AT&T Bell Laboratory, under the direction of Susanne Nagel, has been kind enough to offer to pull preforms into fiber and analyze them until such time as our draw facility is operational. Since this takes of the order of several months, we have decided to wait until such time in the near future that our tower itself will be operational. However, in order to test our deposition facility, we did have one preform drawn into fiber and characterized by the group at Bell Laboratory. The results are shown in figure 1. It is seen that the absorption losses at 1.3 and 1.55 microns are within a factor of two of the intrinsic Rayleigh scattering. This indicates good performance with respect to OH contamination in the fiber. With the establishment of a draw facility within the Laboratory for Lightwave Technology, the time from beginning a preform to drawing it into fiber will be of the order of a few days, thus allowing rapid experimentation and

adjustment of doping concentrations. This will be particularly true for the fabrication of rare-earth fiber lasers, as well as for future work in non-linear frequency doubling in fibers.

The second aspect of this project involves collaboration with Prof. Risen of the Department of Chemistry who has been preparing rare earth glasses to guide us in fiber composition. Some of the first rare-earth glasses fabricated with sol-gel techniques have been recently prepared in his laboratory. These glasses are of interest as a consequence of their large Verdet constant. The following article by Prof. Risen and his students (Mr. Kang Sun has been supported on this research grant) is enclosed. It has been accepted for publication

In summary, progress has been made in the following areas: establishment of our MCVD preform facility with an ability to create state-of-the-art fibers, doping of preforms with terbium (not yet pulled into fibers), and rare earth glasses formed by sol-gel techniques. Future efforts will be to prepare fibers doped with rare earth elements by several techniques, and to continue studies of bulk formation of rare earth glasses.

LOSS MEASUREMENT: CUT-BACK TECHNIQUE

DATA SUMMARY FOR FILE '08201A' :

TEST SET 2
 OPERATOR: KJW
 FIBER ID: BROWN UNIV
 DRAW #: A860820-1
 LENGTH (METERS): 1190
 DIAM. (MICRONS): 191
 TEST #: 1
 DATA DISC: LOSS_2 #6

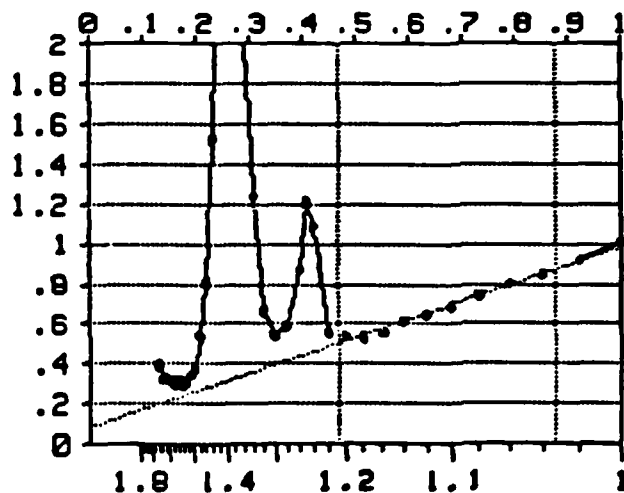
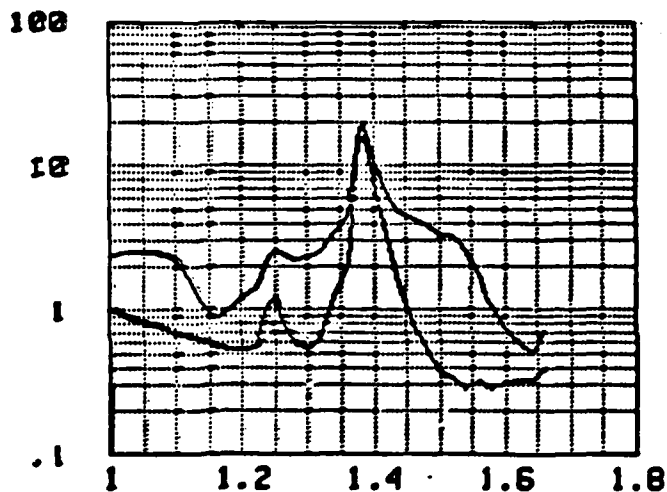
REMARKS: 40 mm DIAM LOOP; 10 m N.E. ; InGaAs DETECTOR

WAVELENGTH (MICRONS)	LOSS (dB/Km)	WAVELENGTH (MICRONS)	LOSS (dB/Km)	WAVELENGTH (MICRONS)	LOSS (dB/Km)
1.660	.389	1.460	.808	1.240	1.084
1.640	.322	1.440	1.526	1.220	.556
1.620	.325	1.420	3.218	1.200	.548
1.600	.317	1.400	8.145	1.180	.531
1.580	.293	1.390	13.950	1.160	.561
1.570	.303	1.386	16.160	1.140	.613
1.560	.317	1.380	15.568	1.120	.648
1.550	.304	1.360	2.057	1.100	.686
1.540	.289	1.340	1.241	1.080	.745
1.530	.302	1.320	.665	1.060	.798
1.520	.339	1.300	.543	1.040	.849
1.510	.347	1.280	.588	1.020	.919
1.500	.373	1.260	.872	1.000	1.004
1.480	.538	1.250	1.210		

MINIMUM LOSS = .289 dB/Km AT 1.54 MICRONS

F.E. DRIFT = +.7 % N.E. DRIFT = +.5 %

MATE FILE IS '08201B' (REPEAT N.E. OF TEST # 2 WITHOUT LOOP)



B = +.081 dB/Km ; A = +.898
 r = +.9941

PARAMETERS FOR THIS TEST:

WAVELENGTHS 1.66 TO 1 MICRONS IN INCREMENTS OF .02
 900 MILLISECONDS DELAY FOLLOWING WAVELENGTH CHANGE
 10 READINGS OF DVM AVERAGED FOR INTENSITY AT EACH WAVELENGTH
 300 MILLISECONDS DELAY BETWEEN DVM READINGS
 200 mV SENSITIVITY AT 'CHECK' WAVELENGTH: 1.55 MICRONS

SOL-GEL PREPARATION OF RARE EARTH SILICATE GLASSES

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Department of Chemistry, Brown University

Providence, Rhode Island 02912

Abstract

Rare earth silicate glasses have been obtained by a sol-gel method starting with the rare earth carbonates of Pr, Dy and Er and TEOS (tetraethoxysilane). Expressed in the form $x \text{ Ln}_2\text{O}_3(1-x)\text{SiO}_2$, the glasses have compositions in the range $x=0.016$ to 0.052 , which corresponds to 1.6 to 5.2 mole percent or up to about 23 weight percent rare earth oxide as determined by electron microprobe. The glasses were produced by densification at 800°C . Infrared and visible spectra and magnetic susceptibilities are reported.

Introduction

The characteristics of binary silica based rare earth glasses are of particular interest for optical applications in which silica based materials with large Verdet constants and lasing ability are required. This is especially important in optical fiber technology, where binary rare earth silicates are needed to create nonreciprocal devices, such as isolators and circulators, and magnetic field sensors. Of course, glasses with these compositions also are of interest in geological, chemical and other optical fields.

Due to the extremely high melting points of rare earth oxides and SiO_2 , however, the preparation of binary rare earth silicates from melts requires temperatures of 1800°C or higher. Moreover, the melt method is limited to compositions for which quench techniques are sufficiently fast to avoid phase separation problems. This has caused experimental difficulties and often lead to low quality glasses. (1).

The sol-gel method provides an approach to obtaining binary rare earth silicates as pure, homogeneous glasses at much lower temperatures than required by conventional melt-quench techniques. There have been several attempts to prepare such glasses using sol-gel methods. Mukherjee, et al (2) prepared glasses by melting compositions which were present originally as crystalline materials or gels, so gels were involved, but since melting was required these cannot be considered sol-gel glasses. Wang and Hench (3) reported the preparation of sol-gel derived silica optical filters, using the DCCA approach, including a rare earth silicate described as a "1% (mol%) Nd silica gel heated to 850°C ." However, it carefully was not described as a glass, and its visible spectrum was found to differ significantly from that of the analogous melt-prepared glass. Thus, it appears that the sol-gel preparation of binary rare earth silicate glasses has not yet been reported.

Previous failure to obtain sol-gel glasses with high rare earth concentration has been encountered either when the metal ions failed to incorporate in the glass network (4) or

when low quality glasses (partially crystallized, opalescent or opaque) were produced (5). The use of drying control chemical additives appears to help overcome the former problem in the case of gels to an extent not fully specified (6).

In order to synthesize high quality binary silicate glasses containing high concentrations of rare earth ions by sol-gel methods, it is necessary to choose the starting materials judiciously, and control the acidity of the reaction medium, the hydrolysis rates of all of the materials, and the drying and desiccation processes very carefully. These restrictions are particularly severe if the preparation is not to require introduction of the rare earth ions in a special form, such as alkoxides, to avoid the use of water.

In this paper we report the preparation of binary rare earth silicate glasses by a sol-gel method. Our method starts with rare earth carbonates and tetraethoxysilane (TEOS). Glasses containing praseodymium, dysprosium and erbium at weight percentages as high as 23% have been prepared and fully analyzed. These rare earth elements were selected to demonstrate the method with ions having a range of sizes and masses.

Experimental

Tetraethoxysilane, $\text{Si}(\text{OC}_2\text{H}_5)_4$ (sometimes abbreviated TEOS), and 99.9% $\text{Ln}_2(\text{CO}_3)_3 \cdot y\text{H}_2\text{O}$ [$\text{Ln} = \text{Pr}$ ($y=8$), Dy ($y=4$), and Er ($y=6$)] were used as starting materials. The water content in the sol was adjusted so that all the $\text{Si}(\text{OC}_2\text{H}_5)_4$ present can be hydrolyzed, but was kept to the minimum needed for the processes used. Ethanol (absolute, 100%) was used for diluting the alkoxide (TEOS). Hydrochloric acid (12M, 37%) was used as a catalyst for hydrolysis and to dissolve the lanthanide carbonates.

In the first step, lanthanide carbonates were dissolved in a minimum of HCl, and the resulting solution was soon added drop by drop to the TEOS-ethanol solution with stirring. The resulting solution (sol) remained transparent through the gel point which indicates its

uniformity and lack of phase separation. The sols gelled in about 6 hours in an open container, and in about 15 hours in a loosely closed container in air, respectively. Gels were aged at 25°C for at least 5 days, and then were heated to 600°C, at a controlled heating rate of 1°C/min., after heating them at 200°C for 2 hours. They then were densified at 800°C for 6 hours to convert them fully to glasses. Finally, the densified glasses were further dried at 800°C for 10 hours to remove residual (0.2–6%) water.

In a typical experiment, 1.2119 g of $\text{Pr}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$ were added to 1.785 g of HCl and 3.664 g H_2O in a Teflon beaker and stirred for 2–4 minutes to allow for the evolution of most of the CO_2 . This solution was added dropwise over 10–15 minutes to a stirred solution made by mixing 10.00 g of TEOS and 10 g of absolute ethanol. This corresponds to 0.004 mole Pr^{+3} and 0.048 mole Si, and should lead to a glass of composition $0.04\text{Pr}_2\text{O}_3 \cdot 0.96\text{SiO}_2$. Its elemental analysis, when dried and densified, showed it to be $0.052\text{Pr}_2\text{O}_3 \cdot 0.948\text{SiO}_2$.

All glasses were examined by x-ray diffraction and shown to be amorphous. The elemental compositions of the glasses were determined to within ± 0.01 weight percent by electron microprobe analysis, calibrated with accurately known standard. The microprobe data were measured with a Cameca Microprobe (take off angle 40°) at an excitation voltage of 20kV and beam current of 15nA. Infrared spectra were obtained on a Digilab FTS-15B spectrometer. The KBr pellet technique was used. At least 200 hundred scans at a resolution of 2 cm^{-1} were signal averaged. Magnetic susceptibility measurements were performed on a Faraday Balance equipped with a Cahn electrobalance (Model RG) at room temperature. Measurements were made at field strength 10.40 kOe and field gradient, $H(dH/dz)$, of 17.93. Thermal gravimetric analysis (TGA) was performed on a System 113 thermal gravimetric analyzer. Visible absorption spectra were obtained on a Cary 17 UV/Visible spectrophotometer.

Results and Discussion

The lanthanide silicate glasses prepared by this method were designed to have 0.9 to 5.2 mole percent rare earth, where the mole percent is given by x in the formula $x\text{Ln}_2\text{O}_3(1-x)\text{SiO}_2$. When they were analyzed after initial densification at 600°C , with about 2 hours at 800°C , the lanthanide and silicon concentrations were slightly less than expected. The materials contained from 0.2 to 6 weight percent of another component, which was assumed to be H_2O , since no chlorine was present. Samples of these materials were studied by thermogravimetric analysis and found to give off volatiles constituting this weight percentage in the $800\text{--}850^\circ\text{C}$ range when heated over about three hours. Therefore the glasses were heated further at 800°C for ten hours and newly analyzed by electron microprobe.

Each glass was analyzed at 10–40 randomly selected $20\text{ }\mu\text{m}$ regions. The analysis at each spot on a given sample gave identical results. The compositions were determined to an accuracy of ± 0.01 weight percent and are given in Table 1. All analyses accounted for 99.5 ± 0.5 weight percent of the glasses in terms of Ln_2O_3 and SiO_2 , and are given in Table 1 in terms of x in $x\text{Ln}_2\text{O}_3(1-x)\text{SiO}_2$.

The fact that the glasses were x-ray amorphous and the fact that all $20\text{ }\mu\text{m}$ spots gave identical analyses, show that these materials are amorphous and homogeneous, with no possible phase separation at a level greater than $ca\text{ }20\text{ }\mu\text{m}$.

The infrared and ultraviolet–visible spectra of the glasses were measured. The infrared spectra of one of the glasses, $x\text{Er}_2\text{O}_3(1-x)\text{SiO}_2$, $x = 0.035$ taken both after initial and final densification are shown in the $500\text{--}1800\text{ cm}^{-1}$ region in Figure 1. The spectrum of the glass taken after treatment at 600°C is shown as a, and that of the same material after being heated at 800°C for 10 hours is given in b. The spectrum of the fully densified glass is similar in appearance to that of amorphous SiO_2 , with medium to strong bands at

ca 810 and 1080 cm^{-1} and a shoulder that becomes pronounced near 1220 cm^{-1} . However, the shapes and relative intensities of these bands differ somewhat from those of SiO_2 , of course, due to the presence of the rare earth ions, but no new separate bands are introduced. This is shown in Figure 2, where the 450–1400 cm^{-1} spectra of a series of dysprosium silicate glasses with increasing Dy content are presented. The main regions of interest are 600–640 cm^{-1} , where the absorbance decreases slightly as Dy^{+3} ions are introduced, and near 900 cm^{-1} , where the absorbance increases significantly. On close inspection of the spectra in Figure 1 and analogous spectra in which the rare earth content is constant, it is seen that the decrease occurs near 620 cm^{-1} as densification occurs, but that no increase occurs near 900 cm^{-1} . Thus, we believe that the small decrease in the 600–640 cm^{-1} region is associated with the network, and that the increase at 920 cm^{-1} is due primarily to the presence of the rare earth ions. Since the 870–930 cm^{-1} region is quite typical for the infrared active M-O stretch of oxygens bound to highly charged metal ions (7), the absorbance increases at 920 cm^{-1} proportional to the Ln^{+3} concentration is assignable to such a vibration. This assignment must be taken to be tentative, however, in light of the well known complexity of silicate spectra.

The glasses treated only to 600°C show evidence of incomplete formation of the network and of the presence of H_2O . Thus, in Figure 1a the band at 1620 cm^{-1} is due to the H-O-H bending mode. It is largely removed by extended heating at 800°C, as shown in Figure 1b. In regions not shown, the 600°C treated glass also shows the presence of water by a broad absorbance in the 3000–3700 cm^{-1} region, which is lost upon treatment at 800°C.

The usefulness of a glass as a Faraday rotator depends on both its absorption spectrum and its magnetic susceptibility. The visible absorbance spectrum also serves as a basis for comparison of the ligand fields of the rare earth ions in these glasses with those in melt-quenched glasses containing them. Although exact comparisons are not

available, spectra of rare earths in glasses with other networks can be used. The spectrum of one of the erbium silicate glasses is shown in Figure 3. The bands correspond to the transitions assigned in Table 2 and compared to the bands reported for erbium borate glasses (8). They correspond quite closely, as do those of the praseodymium silicate glass to the transitions found in Pr^{+3} in the melt prepared phosphate glasses (9). This result can be contrasted to the situation in Nd gels reported by Wong and Hench (3), who found that the spectrum of the gel was quite different from that of the melt-quench glass. Thus, in the sol-gel prepared glasses reported here, the optical absorptions of the rare earth ions are as expected for fully formed glasses.

The magnetic properties of the rare earth glasses are central to their potential application. The magnetic susceptibility, χ , is strongly related to the Verdet constant, which measures the magnitude of the Farady effect. The magnetic susceptibilities of these sol-gel prepared glasses are presented in Table 1. The values of χ reported here are corrected for diamagnetic contributions, and represent the paramagnetic susceptibilities associated with the rare earth ions. There is a linear relationship between χ and the concentration of each type of rare earth ions. This means that the rare earth silicate glasses are magnetically dilute, or, similarly that the rare earth ions are not coupled magnetically in the network at room temperature. This is the expected behavior for rare earth ions, whose magnetic properties are due primarily to unpaired electrons in f orbitals. The magnetic moments are quite close to those expected for the $^3\text{H}_4$ state of Pr^{+3} , the $^6\text{H}_{15/2}$ state of Dy^{+3} and the $^4\text{I}_{15/2}$ state of Er^{+3} (10).

The key to success in this sol-gel method involves control of the introduction of the rare earth ions. Analogous preparations in which there was significantly more H_2O or in which the rare earth ions were introduced as their soluble chlorides or nitrates were not successful. Moreover, if the initially dissolved rare earth carbonate was allowed to stand in air for more than an hour, the efficiency of introduction of the ions (the concentration

attainable) decreased significantly. From these results, we infer that the release of CO_2 by acidification of the carbonate, under the conditions used, leaves the rare earth ions essentially as hydrated ions which do not form hydroxides, because of the acidity, or other unreactive or insoluble ions within the time required for addition to the alcoholic TEOS solution. Thus, the key seems to be to obtain hydrated ions in concentrated solution (so there is as little water as possible) and to react them with TEOS before they undergo reactions with Cl , H_2O or O_2 to form unreactive complexes. The stoichiometry is crucial as well, because increasing the amount of H_2O used to dissolve the rare earth ion serves to limit the concentration of Ln^{+3} in the glass by increasing the amount of TEOS solvolyzed. Thus, the stoichiometry and the kinetics of the initial stages of reaction must be controlled. Recognizing the importance of the metal ion coordination chemistry is even crucial to preparing transition metal silicate glasses.

The analysis of these materials not only provided the Ln^{3+} , Si and O contents, it also showed that no C or Cl remained in the glasses. This means that HCl is lost completely and that the heating schedule lead to complete evaporation of the ethanol present both as solvent and as a product of solvolysis of the TEOS. The water present in the system was lost more slowly, as indicated by the fact that the last 0.2 to 6 weight percent was removed at 800°C . Presumably it also would be removed, but more slowly, at 600°C .

In this work the objective was to prepare glasses of controllable composition in the 0–6 mole percent Ln_2O_3 range by a sol-gel method, and it was found possible to do so without heating above 800°C . Such lanthanide concentrations represent the range over which a region in an optical fiber would be expected to vary as it progresses radially from a concentrated region to a pure silica region. Moreover, it is near a eutectic at which congruent melting could occur without phase separation, including that due to liquid-liquid microphase separation. Since it was not the objective to make monolithic structures, the gel was broken up from time to time during densification (after gel formation) to enhance

evaporation of volatile components. This is not necessary in principle, so other macroscopic forms are possible. The materials obtained ranged from small particles to pieces about 0.5 cm in diameter.

Conclusion

Pure binary rare earth silicates have been obtained with Pr, Er, and Dy in the 1-6 mole percent Ln_2O_3 range, and shown to be amorphous, anhydrous and analyzed to within 0.1 weight percent. Their infrared and visible spectral properties are as would be expected for homogeneous melt-quenched glasses, and their magnetic properties show that the paramagnetism is that of magnetically dilute ions.

Acknowledgements

This work was carried out in collaboration with Professor Theodore Morse under AFOSR Contract AFOSR-85-0304. We are grateful to Professors Morse, M. Rutherford and P. Hess and to Mr. Adam Ellison for helpful discussions. We gratefully acknowledge the cooperation of Professor A. Wold and Dr. Z. Zhang in obtaining magnetic measurements and of Dr. Joseph Devine in carrying out the electron microprobe studies.

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Figure Captions

- Figure 1 Infrared spectra of ErSi-004 ($0.035 \text{ Er}_2\text{O}_3 \cdot 0.965 \text{ SiO}_2$) in the $500\text{--}1800 \text{ cm}^{-1}$ region in KBr pellets. Here (a) is that of the partially densified materials, treated to 600°C , leading to ErSi-004, and (b) is that of ErSi-004.
- Figure 2 Infrared spectra of four dysprosium silicate sol-gel glasses, $x\text{Dy}_2\text{O}_3(1-x)\text{SiO}_2$, with $x = 0.01, 0.02, 0.033$, and 0.043 , in the $450\text{--}1400 \text{ cm}^{-1}$ region in KBr pellets.
- Figure 3 Visible absorbance spectrum of ErSi-002 ($0.020\text{Er}_2\text{O}_3 \cdot 0.98\text{SiO}_2$). The spectrum was measured by transmission through a piece measuring about 3 mm on a side.

Table 1

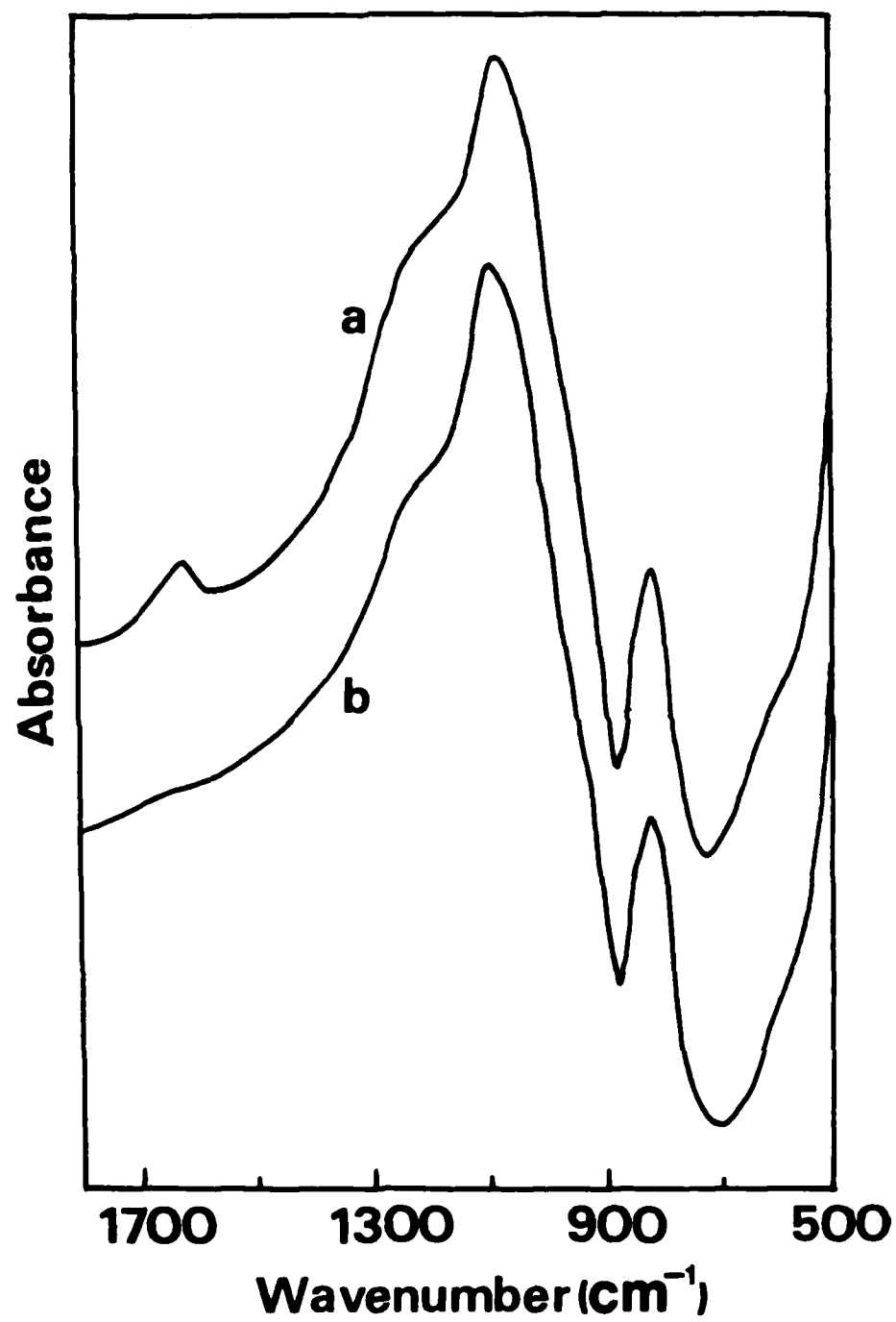
Compositions and Magnetic Susceptibilities of
Rare Earth Silicate Glasses, $x\text{Ln}_2\text{O}_3(1-x)\text{SiO}_2$

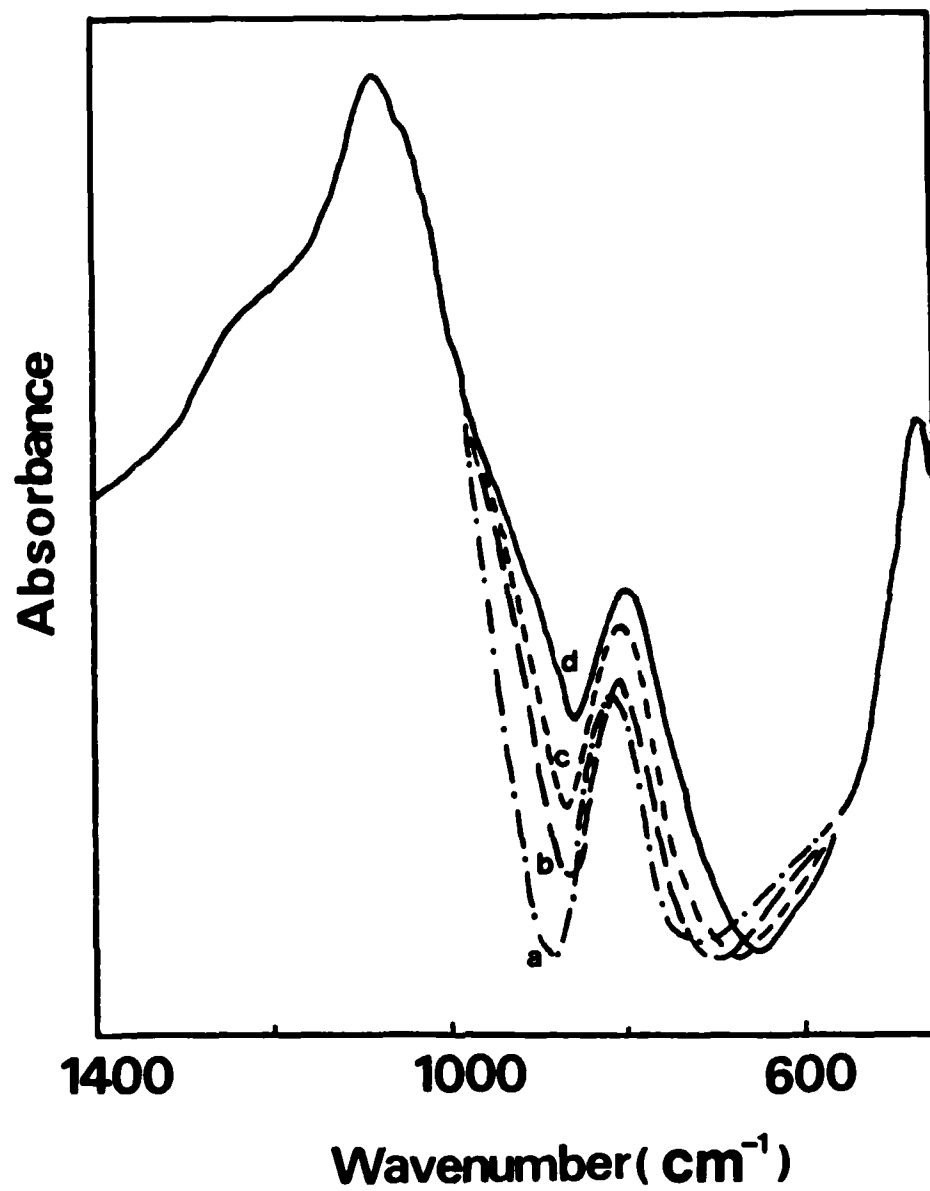
Glass No.	$x(\text{mol}\%)$	$\chi(10^{-3}\text{emu/mol})$
PrSi 002	0.027	0.28
PrSi 004	0.052	0.52
ErSi 001	0.016	1.23
ErSi 002	0.020	1.51
ErSi 004	0.035	2.71
DySi 001	0.009	0.87
DySi 002	0.020	1.84
DySi 003	0.033	3.01
DySi 004	0.042	3.86

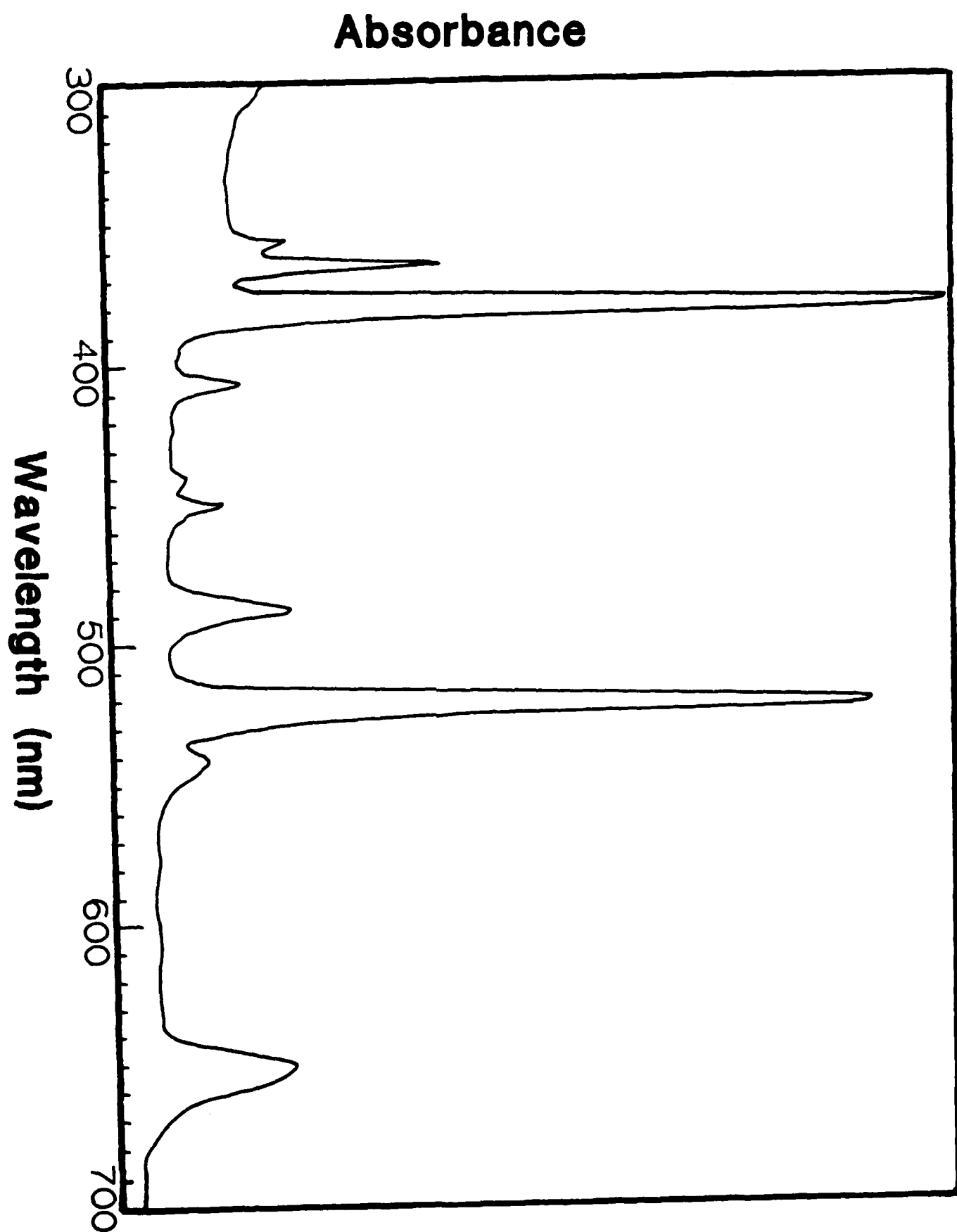
Table 2

**Visible Range Absorptions of Erbium and Praseodymium
Silicate Glasses**

Glass	Observed Band (nm)	Assignment Observation	Analog
ErSi 002	357	$^2G_{7/2}$	(8)
	366	$^2K_{15/2}, ^2G_{9/2}$	
	378	$^4G_{11/2}$	
	407	$^2H_{9/2}$	
	443	$^4F_{3/2}$	
	451	$^4F_{5/2}$	
	488	$^4F_{7/2}$	
	521	$^2H_{11/2}$	
	543	$^4S_{3/2}$	
	651	$^4F_{9/2}$	
PrSi 002	447		(9)
	473		
	485		
	590		







Laboratory for Lightwave Technology
Division of Engineering, Brown University
Providence, R.I. 02912

I. Introduction

A Laboratory for Lightwave Technology has been established within the Division of Engineering at Brown University. At the present time, we possess the first facility at a U.S. university capable of producing state-of-the-art optical fiber preforms, the rods from which optical fibers are subsequently pulled. Our preform rods are analyzed with a York Technology Preform Analyzer in our Fiber Characterization Laboratory. In addition, a DoD Equipment Grant has allowed the purchase of a complete draw facility. This equipment presently represents a total in excess of two thirds of a million dollars in our laboratory alone, and it is supplemented by NMR and Raman equipment for bulk characterization of inorganic glasses in the Departments of Physics and Chemistry as well as the Central Facility of the Brown University Materials Research Laboratory.

Our research program emphasizes new techniques of preform fabrication, the study of specially doped preforms for use as sensors and polarization maintaining fibers, and studies of stress induced effects in fibers. With members of the physics and chemistry departments, we are also engaged in NMR and Raman studies of the incorporation of novel as well as traditional dopants and how processing affects the manner in which these dopants are incorporated into a glass matrix. Emphasis is placed not on the traditional telecommunications fiber, but on special fibers and fibers associated with sensor applications. Such fibers will become increasingly useful within the next decade in a host of situations that range from nondestructive monitoring of composite materials (with imbedded fibers), biomedical uses, to applications in combustion research. Optical fibers, because of their lower weight/information-channel, are already beginning to play a significant role in the instrumentation and control of aircraft and spacecraft.

The activity at Brown in this area was initiated by Prof. T.F. Morse through his interest in laser enhanced thermophoresis. Studies have shown how aerosol-laser interactions can significantly increase thermophoretic deposition in the MCVD process. However, with the acquisition of fiber preform equipment, and the impending installation of a draw facility, the focus of the laboratory has been broadened to include a host of fundamental aspects of lightwave science and technology. We believe that one of the more important areas of future fiber research will involve the union of microelectronics with fiber devices. Research is in progress that involves matching the fast electronic switching capabilities of strained super-lattice devices with fiber technology at GaAs wavelengths. The thrust of this research will be in the ultimate implementation of fiber devices with new semiconductor technology.

The use of specialty optical fibers as sensors in such disparate fields as solid mechanics, chemical species detection, biology and medicine, creates a seemingly endless list of possible areas of application. We are clearly not in a position to pursue active research into all of the areas in which we believe optical fibers will play an increasingly important role. Our main thrust will be to develop a fundamental understanding of the material and structural attributes of specialty fibers. We also hope to initiate a program in non-linear effects in fibers and to study the effects of novel dopants on Raman gain. Our facility places us in a unique position among universities to carry out such activities.

A series of proposals have been written and submitted to various agencies with the intention of supporting joint activity outside of our group in the Division of Engineering. Funds generated from these proposals have allowed the nucleus of a Laboratory for Lightwave Technology to be formed. Participating faculty members will share equipment as well as the advising of graduate students. At

the present time, there are four Ph.D. students within the Division of Engineering and one in the Department of Chemistry associated with the activities of our laboratory. It is expected that this number will double in the near future. Among the participants in our activity are a former student from Solid Mechanics who is now an Associate Professor of Mechanics at the University of Illinois, Prof. K.S. Kim, an expert in both optics and solid mechanics, Prof. J. Cipolla, (Mechanical Engineering, Northeastern University) who has been closely involved with the theoretical aspects of this work from its inception, and two professors of chemistry (one of them an expert in amorphous glasses, Prof. W. Risen, and Prof. A. Wold, a chaired professor and editor of the Journal of Solid State Chemistry). Additional faculty who will participate are Prof. N. Lawandy, from electrical engineering who has been presented a Presidential Young Investigator award from the National Science Foundation, two professors from the Fluid Mechanics, Thermodynamics and Chemical Processing group; Prof. B. Caswell, and Prof. E. Suuberg, and Prof. P. Bray, a chaired professor from the physics department specializing in NMR studies of glasses. All will all be contributing their expertise toward increasing our understanding of various materials and fabrication problems as well as applications of lightguides. Prof. Stiles (strained super lattice semiconductors), Prof. Nurmikko, (ultra-fast optical processes in semiconductors), and Prof. Rosenberg (fast electronic devices) are participating in a cooperative program involving semiconductor/fiber devices. We are also collaborating on some novel concepts of soot deposition with Prof. M. Fiebig of the Ruhr Universitaet, Bochum, Germany, as well as with Prof. G. Schiffner, of the Optoelectronics Department at Bochum.

c. Current Topics of Investigation

1. RARE EARTH VAPOR PHASE DOPING OF PREFORMS

There is great interest in the doping of fiber preforms with rare earth elements, and the AFOSR (Physics Branch, \$140,000) is supporting a joint project on this topic with Prof. Risen of the Department of Chemistry. These rare earth elements are difficult to obtain in the vapor phase, and we will be taking two different routes toward their incorporation. First, however, it is perhaps appropriate to discuss, albeit briefly, the motivation behind this project. When light propagates through a glass doped with these elements its electric field vector rotates by an amount proportional to the strength of an external magnetic field and the length of interaction. The constant of proportionality is called the Verdet constant, which is large for the rare earth elements. By sensing the rotation of the field, fibers doped with such materials can be used as electric and magnetic field sensors. In addition, the rotation of the electric field within the fiber (in the presence of a magnetic field) allows the creation of non-reciprocal devices such as isolators and circulators, which are now in common use in the microwave region. One of the possible barriers to the fabrication of such devices is the difficulty of incorporating the lanthanide elements into a silica based glass in the vapor phase. The focus of this research will be to determine inorganic routes to the vapor phase incorporation of the rare earth elements into a silica based optical fiber preform. This is desirable, since high quality fibers have been produced only from vapor phase deposition techniques. We will react terbium with chlorine to produce a terbium chloride aerosol that will be transported in an oxygen stream to react at the burner and thermophoretically deposit terbium oxide along with the silicon dioxide in a typical MCVD configuration. The preforms that result from this process will be analyzed with a micro-Raman probe, and the composition and incorporation of Tb^{3+} ions compared with glasses of similar composition that Prof. Risen will make in his laboratory in the Department of Chemistry. Work is in progress. We also note that fibers doped in this manner will be excellent candidates for the study of non-linear Raman gain. This program is, in some aspects, similar to that at the University of Southampton in the institute of Prof. A. Gambling.

2. LASER ENHANCED FABRICATION PROCESSES

Supported by NSF, \$223,854, three years, renewal at \$222,000, three years. We have shown that laser heating of the aerosol deposited in the MCVD (Modified Chemical Vapor Deposition) fabrication of the preforms from which optical fibers are formed can have a dramatic effect on both the rate and quality of deposition. With new equipment that will allow us to create state-of-the-art optical fiber preforms, we plan to study the effects of laser enhanced thermophoretic deposition on optical fiber preforms and the fibers pulled from these preforms. In addition, we will study the collapse rate of preform tubes with the addition of axial laser radiation from a 250 W Model 41C Coherent Radiation carbon dioxide laser. We plan to examine this phenomenon experimentally and theoretically. Increasing the diameter of preform tubes to obtain more fiber can increase the time of tube collapse considerably, and a study of the influence of internal laser heating may yield information on how this step in optical fiber fabrication can be shortened. In addition, we plan a series of double tube deposition experiments with our new equipment that will complement some theoretical work being carried out by Prof. M. Fiebig, of the Ruhr University, Bochum. We are concerned with the manner in which laser heating will affect the incorporation of dopants into the glass, and as noted in collaborative work below, other diagnostic techniques will be used to compare the differences between crucible and vapor deposited glasses. The theoretical aspects of this part of our research will be carried out in collaboration with Prof. Cipolla, of the Mechanical Engineering Department of Northeastern University, and Prof. B. Caswell, of the Brown Division of Engineering.

3. NMR STUDIES OF VAPOR DEPOSITED PREFORMS AND FIBERS

Proposal is in preparation with Prof. P. Bray, Physics Department. Several techniques will be used to gain an assessment of the structure of the preform tubes that result from our research. One of these, Nuclear Magnetic Resonance (NMR), will be employed in a fundamental study of the incorporation of dopants into optical fiber preforms created with MCVD. Prof. P. Bray will be guiding this aspect of the program. It is of great interest to characterize and possibly explain the differences between glasses formed from the melt and vapor phase deposited glasses.

NMR techniques will be used to study local structure and bonding in glass fibers produced in the Laboratory for Lightwave Technology. Measurements of dipolar broadening, quadropolar effects, chemical shifts, and spin-lattice and spin-spin relaxation times will be used to determine whether dopants (or glass components) are aggregated or dispersed, and to characterize the bonding configurations and structural groupings formed in the glasses.

Studies are already in progress involving boron and fluorine in fibers provided from industrial sources. Detailed studies of phosphorous in silica fibers have been published from another laboratory. Since the process for producing fiber preforms can yield materials not achievable from the melt, a new and large family of elements can be studied by NMR to determine the coordination, bondings, structural groupings, and other characteristics on an atomic scale that determine the microscopic characteristics of the fiber. A fundamental study of the incorporation of germanium is also contemplated.

4. POLARIZATION MAINTAINING FIBERS

Submitted to the National Science Foundation, (\$875,990, three years). A joint University/Industry Cooperative Program with Avco-Everett Research Laboratory and the University of Illinois. The impetus for polarization maintaining fibers comes from two different sources. Perhaps the most immediate of these is in optical fiber sensors in which deviations from a specific state of polarization may be associated with the presence, for example, of an electric or magnetic field. It is necessary for these fibers to maintain polarization in the absence of the external disturbance that they attempt to measure (i.e., magnetic or electric field). A further need for high

quality polarization maintaining fibers might be in some future coherent communications system.

Polarization preservation in fibers may be generically divided into two different types: low birefringence, and high birefringence. If we can envision a low birefringence single mode fiber that in some sense is "perfect" with regard to uniformity of dopant and uniformity of external influences on the fiber, then this ideal device will maintain its polarization. Unfortunately, there are a myriad number of internal as well as external influences that serve too well to disturb this ideal depiction. Any physical imperfections in the fiber itself, as a consequence of lack of circularity from some quirk in the production process, or any micro-bubbles or cracks in the fiber will cause a random interaction between the two propagating modes of different polarization that are present in a single mode fiber, and the polarization maintaining characteristics of the fiber will be lost. In addition, any asymmetrical lateral stress, of either internal or external nature, will also destroy polarization maintaining features. For example, a tiny axial scratch on the surface of a drawn fiber produces a huge stress singularity if the fiber is subjected even to a small twist. All of these effects influence the polarization coupling of the two modes that propagate in the fiber and degrade the ability of the fiber to maintain a single polarization.

Since low birefringence fibers can be affected in a number of ways by internal imperfections or external disturbances, we consider an alternate approach taken by other researchers: that is, to increase the birefringence of the preform, and hence the fiber, through the deliberate introduction of a high degree of internal stress and azimuthal asymmetry in the fiber. It is upon this latter aspect that this research shall focus. This work will be carried out in cooperation with Prof. K.S. Kim, of the University of Illinois. Implementation of these fibers in sensor devices will be carried out in conjunction with the fiber sensor group at the Avco-Everett Research Laboratory, under the direction of Dominique Dagenais.

To insure that a high birefringence fiber has the capability of maintaining a specific state of polarization, it is necessary that some asymmetry in the azimuthal direction be included in the fiber. There are several ways in which this may be done. Japanese manufacturers, in particular Sumitomo and Hitachi, rely on an elliptical core within a circular cladding. Depending upon the cladding material and profile, the fast axis may be along either the semi-major or the semi-minor axis. Bell Laboratories has recently reported on the polarization preserving characteristics of a fiber pulled from a preform that had been flattened on two sides before being pulled. This seemed to have the advantage that the preferred axis could be located from the external shape of the pulled fiber. Another method, introduced by the group under Professor A. Gambling at the University of Southampton, England, attempts to make use of the mechanics of stress induced birefringence in fibers in order to create the desired degree of azimuthal asymmetry. This is done by localized heating to remove dopants leaving an azimuthally asymmetric dopant profile in the preform. We plan to investigate multi-dimensional effects of stress birefringence in preforms and fibers. Our theoretical program will be complimented by experimental studies employing laser etching of the preform to achieve a highly controlled degree of azimuthal stress asymmetry in the preforms fabricated in our laboratory.

5. A ZINC CHLORIDE FIBER

Zinc chloride, which is an extremely hygroscopic material, has the ability to form a low temperature glass. It transmits best in the mid infrared, and its infrared edge absorption allows transmission up to 10.6 microns. It was recently learned that Bell Laboratories is beginning to look at this system again because of its possible suitability as a low loss fiber. We are investigating the possibility of vapor phase deposition of this material via a suitable organic precursor with subsequent removal of water by flowing HCl through our deposition system. A possible substrate tube would be polyaniline fluoride which is quite impervious to water. This material could be used as a substrate in an MCVD process for obtaining dry, glassy zinc chloride that could result in a graded index preform (when doped with barium chloride).

6. NON-LINEAR INTERACTIONS IN GLASSES AND FIBERS

The following topics of research will be carried out with Prof. N. Lawandy, and a proposal to DoD is in progress. With the ability to dope fiber preforms with special elements, it is of interest to study non-linear effects in fibers. As a consequence of their small core, it is possible to achieve non-linear effects with modest laser powers. The two main thrusts which we would like to address are nonlinear frequency generation in optical fibers and nonlinear propagation and material damage in glasses and fibers. The first of these efforts will focus on understanding the behavior of the nonlinear second order susceptibility of glasses using tunable stimulated scattering in fibers with emphasis on coherent phonon contributions to the response. Secondly we will study the effects of explosive phonon build up on problems of laser induced damage in glasses. This effort will utilize self focusing effects and filament characteristics to study the problem.

i. RAMAN AMPLIFICATION IN SINGLE MODE FIBERS WITH A TUNABLE ALEXANDRITE LASER PUMP TO PROBE THE NONLINEAR SUSCEPTIBILITY OF GLASSES AND GLASS FIBERS.

The use of intense pump sources to generate gain at the sum and difference frequencies of the pump and a molecular resonance has been well studied. This effect has been shown to produce enormous gains at the lower Stokes frequency in liquid and solid media due to the high atomic densities available. Recently, several experiments have demonstrated that optical fibers are excellent candidates for generating Stokes gain and lasing at the down converted frequency. This is primarily due to two reasons: 1) fibers may support several tens of watts of pump power in extremely small cross sectional areas (20 microns) evolving the large intensities required for nonlinear frequency generation, and 2) they may provide extremely long interaction lengths in a small volume (1 km of fiber may be wrapped into a spool that fits into a movie film container).

Raman amplification has been demonstrated at 1.2 microns with a 1.06 micron pump by Koepf, et. al, and has generated a gain of 10^3 in 1 km with only 1.4 Watts of pump power. This experiment has defined the other physical mechanisms, such as Brillouin scattering effects, which limit the gain, allowing for a reasonable engineering design to achieve a given power output at the desired wavelength.

The recent development and characterization of Alexandrite lasers has resulted in a tunable intense source between 7000-8000 Å. The tunability and intensity will allow for the experimental probing of the molecular Raman scattering cross sections behavior in glasses by frequency resolved gain and pump measurements. The work will be aimed at understanding the effects of other coherent processes such as stimulated forward and backward Brillouin scattering on the stimulated Raman scattering (SRS) process. In particular, the quenching of phonon processes in glasses may be studied in this way by temperature dependent experiments on SRS gain.

ii. SELF FOCUSING AND LASER INDUCED DAMAGE

It is well known that materials which have positive Kerr nonlinearities result in self focusing and filament formation. The effect is due to the positive intensity dependent lens which results in a Kerr medium due to the peaked transverse intensity distribution of the propagating beam. This effect has resulted in light filaments less than 1 micron in diameter at visible wavelengths. This focusing results in damage in most materials, and the phenomenon is not understood. The primary problem lies in the fact that not enough power is absorbed to result in simple thermal damage. We would like to study the problem with a focus on nonlinear coherent generation of phonons at the self focusing catastrophe point. The generation rate of phonons has been shown to be unstable in SRS due to the boson behavior of the phonons. This approach to the damage problem could be studied in glasses with both amorphous and crystalline structure in order to assess the effects of coherently induced phonons in the optical damage problem. Needless to say, self focusing of this magnitude could play

an important role in coupling into fibers for energy transfer.

7. MCVD DEPOSITION AND GRADIENT INDEX LENSES

Proposal pending at ARO, Durham (\$140,000, 12 months). The use of modified chemical vapor deposition has been extensively used in the fabrication of highly structured gradient index fibers. We propose to examine the suitability of this technique to fabricate gradient index lenses. That is, the preform would be sliced up and not drawn. For such an application it is possible to resort to dopants that, by virtue of their higher absorption are not suitable for long range fiber transmission, but that would be well suited for gradient index lenses. This raises the interesting possibility of organo-metallic doping of preform rods to achieve a high index difference suitable for such lenses. In order for successful progress to be obtained in this area, a deeper understanding of the nature of the "deposition wiggles" on the MCVD preform must be in hand. We will engage in modeling work on both the deposition details as well as on the effects of consolidation modifying the diffusion of dopants through the preform. This work is being performed in cooperation with Prof. D. Moore, of the University of Rochester, Institute of Optics, who has been advising us on gradient index lenses.

8. HIGH TEMPERATURE COATINGS FOR SILICA BASED FIBERS

A proposal is in progress to NSF, NASA and ONR, with Prof. A. Wold, Department of Chemistry and Prof. S. Nutt, Materials Science Group, Division of Engineering. Although silica based fibers can withstand temperatures of the order of 1,000 °C, hermetic coatings fail at much lower temperatures. The highest temperature fibers presently available are gold coated, suitable to approximately 650 °C. A more desirable coating would be a dielectric of sufficient thickness and toughness to protect the fiber from abrasion. The use of such fibers would be in pyrometry and in sensor and control system fibers in jet engines.

We propose to study the coating of fibers with an extremely thin barrier of CVD deposited alumina to assure a hermetic seal. On a draw tower, pulling rates would be such that only a thin layer could be deposited in this manner. Since such a layer would not protect a fiber from abrasion, we wish to study the application of a subsequent thicker coating using a sol-gel on-line process. The higher quality CVD deposited barrier layer would protect the silica based fiber from moisture, and, at the same time, it would form an ideal substrate for the thicker abrasion resistant sol-gel layer. Prof. A. Wold has had considerable experience in the coating of alumina onto various substrates for electronic applications using both CVD and sol-gel processes. Prof. Nutt's specialty is the microscopic study of interfacial phenomena. We also wish to consider the suitability of other ceramic coatings for compatibility of sensor fibers to be implanted in high temperature "next generation" ceramic and composite materials.

In summary, the Laboratory for Lightwave Technology will engage in research in the following areas.

1. Novel preform processing techniques, laser assisted thermophoretic deposition, and laser assisted collapse.
2. Rare earth doping of fibers, fiber sensors, non-reciprocal devices using fibers (isolators, circulators), tunable fiber lasers.
3. Optimization of fiber designs (geometry and doping) for specific sensor applications.
4. Non-linear effects in optical fibers.
5. Use of organic precursors in structuring a ZnCl_2 fiber for surgical applications.

6. Studies of MCVD deposition for application to gradient index lens fabrication.
7. Fundamental studies of optimum stress distributions for polarization maintaining fibers. Techniques of internal laser etching of preform.
8. High temperature dielectric coatings for optical fibers suitable for on-line coating.

III. Equipment

Our laboratory for Lightwave Technology within the Division of Engineering is particularly suited for experimentation involving the preparation of special optical fiber preforms. We have just installed an optical fiber preform facility that includes (from Special Gas Controls, Melbourn, England) an ultra dry gas system, automatic computer control system, process monitor control, double carriage, double burner, universal MCVD glass lathe with microprocessor lathe controller, a freon drier, a chlorine drier, a dual channel carrier gas purifier, an effluent scrubbing system, and a burner temperature control system. (\$250,000) Ours will be the first university laboratory in the U.S. with the ability to design and fabricate optical fiber preforms from the vapor phase. We have also installed a York Technology preform analyzer. (\$80,000) This is an important complement to our present apparatus. Further, we have been received a \$275,000 grant from the Department of Defense. The installation of a complete draw facility as well as additional fiber characterization equipment is in progress.

A Micro-Vax II has been installed on an Ethernet link to a series of larger Digital Equipment machines, and this will be used to control and coordinate some of our laboratory activities. In addition, we have two Model 41C Coherent Radiation carbon dioxide industrial lasers. The output is approximately 270 W. One laser was a gift of the IBM Corporation to our laboratory, and we have just been given another laser of the same type by the Florsheim Shoe Company of Chicago, Ill. This will allow increased efficiency in our laboratory, since several experiments employ these high power lasers. We also have a smaller "home built" carbon dioxide laser, and a pulsed 1 J carbon dioxide TEA laser. Further, there are two fume hoods, including a floor "walk in" model. Other equipment in this laboratory consists of oscilloscopes, detectors, pumps, He-Ne lasers, and an optical table. There is also a full machine shop available for any work that might need to be done in the construction of equipment.

In addition to the equipment cited above in our laboratory, the laboratories of Prof. Risen and Bray contain considerable equipment used for glass research. These include NMR spectrometers used primarily for ^7Li , ^{11}B , ^{17}O , and ^{19}F . A new FTNMR will be truly multinuclear, of great importance for the rare earth elements we wish to consider. (Prof. Bray). In the laboratory of Prof. Risen, there is a new Spex Ramalog MicroRaman spectrometer with Spectra Physics 4 W (all lines) Ar^+ laser. The MicroRaman has a spatial resolution of 2 microns. In the infrared and Far infrared there is a Digilab FTS15B Fourier Transform Infrared Spectrometer that can take relatively good spectra between $50\text{-}4000\text{ cm}^{-1}$. In addition, MRL Optical Facility has purchased a BOMEM DA3.1 FTIR with its initial configuration having a range of $30\text{-}40,000\text{ cm}^{-1}$ as well as microscopic infrared capabilities. There are a number of high temperature furnaces, the most advanced of which is a CM Rapid Temp 1700B Furnace with a sustained temperature to 1600°C . In addition, within the MRL facility is equipment for the measurement of fast optical processes, electron microscopes, ion microprobes, as well as a complete microelectronics laboratory for vapor deposition and encapsulation. This latter equipment may play a role in future structuring of devices on fibers.

Our present equipment provides a natural complement to the extensive MRL bulk characterization facility for the physical properties of glasses. We will be able to analyze our preforms with a sophisticated FTNMR. This will be particularly important for studies in which we wish to determine the manner in which dopants are incorporated into vapor phase deposited

preforms. Further, a micro Raman probe in the laboratory of Prof. Risen of the Chemistry Department will enable us to scan preforms and fibers with a high degree of spatial resolution. This equipment will prove of great value in detailed characterization of the preforms and fiber samples that are produced in our laboratory. We will be able to produce new glass structures and compositions not attainable with crucible techniques. The close cooperation of individuals within the MRL inorganic glass thrust area as well as other groups from within the Division of Engineering will prove invaluable to the success of our program.

IV. Summary

We have assembled a unique group of experts who can make significant contributions to many aspects of lightwave science and technology. With the first vapor phase preform capability at a U.S. university, and funds available for a complete draw facility, we are able to complement the inorganic glass thrust area of the Materials Research Laboratory at Brown to study the influence of processing on glass properties and structure. In addition, cooperative research with members of the Physics department as well as electrical engineering, may lead to new and interesting semiconductor/fiber devices.

Recent Publications

1. "Laser Modification of Thermophoretic Deposition", *J. Colloid. Interfac. Sci.*, with J. Cipolla, Jr., vol. 97., no. 1, January 1984, p. 137.
2. "Laser Induced Natural Convection and Thermophoresis", (with C.Y. Wang and J. Cipolla, Jr.), *Interfacial Transport Phenomena*, p. 13, J.C. Chen and G.S. Bankoff, editors, A.S.M.E., 1983, see also *J. Heat Transfer*, Transactions of the ASME *J. Heat Transfer*, February 1985, vol. 107, p 161.
3. "Laser induced Thermophoresis and Particulate Deposition Efficiency", (with C.Y. Wang and J. Cipolla, Jr.), *Interfacial Transport Phenomena*, p. 21, J.C. Chen and G.S. Bankoff, editors, A.S.M.E., 1983, see also *J. Heat Transfer*, Transactions of the ASME, February 1985, vol. 107, p. 105.
4. "Heat Transfer in An Absorbing Aerosol", (with J. Cipolla, Jr.), A.S.M.E. Publication, presented at ASME/AICHE Heat Transfer Meeting, Seattle, Wa., June 1983.
5. "One Dimensional Unsteady Thermophoretic Motion", (with D. Girardin, N. Streessing, and J.W. Cipolla, Jr.), A.S.M.E. Publication, presented at ASME National meeting, Boston, Mass., November 1983.
6. "Laser Enhanced Thermophoretic Deposition", (with J.W. Cipolla, Jr.), *Third Symposium on Lasers and Applications*, I.I.T. Kanpur Press, Kanpur, India, 1983.
7. "Thermophoresis in an Absorbing Aerosol: Time Dependent Studies"; w. J.Cipolla, Jr., submitted to *Physics of Fluids*.
8. "Thermophoretic Transport in Laminar Tube Flow of an Absorbing Aerosol", with Ravikumar, J. W. Cipolla, Jr, A.S.M.E. Publication 84WA/HP44.
9. "Laser Induced Buoyancy and Forced Convection in Vertical Tubes", with D. DiGiovanni, C.Y. Wang, and J. Cipolla, Jr., in *Natural Convection: Fundamentals and Applications*, edited by W. Aung and S. Kakac, Hemisphere Press, 1984.
10. "Laser Induced Natural Convection and Thermophoresis", (with C.Y. Wang and J. Cipolla, Jr.), *J. Heat Transfer*, Transactions of the ASME, February 1985, vol. 107, p 161.
11. "Laser induced Thermophoresis and Particulate Deposition Efficiency", (with C.Y. Wang and J. Cipolla, Jr.), *J. Heat Transfer*, Transactions of the ASME, February 1985, vol. 107, p. 105.
12. "Laser Enhancement of Thermophoretic Deposition Processes", (with D.Giovanni, C.Y. Wang, and J. Cipolla, Jr), *Journal of Lightwave Technology*, Vol. LT-4, no. 2, p. 151, February 1986.

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